

**CONDITIONS OF CORE FORMATION IN THE EARLY EARTH: SINGLE STAGE OR HETEROGENEOUS ACCRETION?** K. Righter<sup>1</sup>, <sup>1</sup>NASA Johnson Space Center, 2101 NASA Parkway, Houston, TX 77058; [kevin.righter-1@nasa.gov](mailto:kevin.righter-1@nasa.gov).

**Introduction:** Since ~1990 high pressure and temperature (PT) experiments on metal-silicate systems have showed that partition coefficients [D(met/sil)] for siderophile (iron-loving) elements are much different than those measured at low PT conditions [1,2]. The high PT data have been used to argue for a magma ocean during growth of the early Earth [3,4]. In the ensuing decades there have been hundreds of new experiments carried out and published on a wide range of siderophile elements (> 80 experiments published for Ni, Co, Mo, W, P, Mn, V, Cr, Ga, Cu and Pd). At the same time several different models have been advanced to explain the siderophile elements in Earth's mantle: a) shallow depth magma ocean 25-30 GPa [3,5]; b) deep magma ocean; up to 50 GPa [6,7], and c) early reduced and later oxidized magma ocean [8,9]. Some studies have drawn conclusions based on a small subset of siderophile elements, or a set of elements that provides little leverage on the big picture (like slightly siderophile elements), and no single study has attempted to quantitatively explain more than 5 elements at a time.

The purpose of this abstract is to identify issues that have lead to a difference in interpretation, and to present updated predictive expressions based on new experimental data. The resulting expressions will be applied to the siderophile element depletions in Earth's upper mantle.

**Background and previous issues:** There are a number of factors that have led to diverging interpretations of experimental data. Three of these are summarized here – their impact on the modeling results will become clear in the results section.

**Issue 1:** The importance of variable silicate melt composition. Some studies have concluded that melt composition is not an important control on D(met/sil) [6], or have ignored this variable altogether [10]. In fact, the change in D(Ni) and D(Co) ascribed to pressure in the dataset of [10] are coupled to changes in melt composition. The decreases observed for D(Ni) and D(Co) and due to silicate melt becoming depolymerized, are also observed for other elements. But this effect cannot be generalized, as there are just as many elements that exhibit an increase in D(met/sil) as peridotite melt compositions are approached [11]. Furthermore, some elements show a strong affinity for CaO compared to MgO [12], but standard melt structural parameter NBO/T cannot distinguish between these two network modifiers. As a result, the best modeling approach is to use oxide mole fractions which can help to unravel the competing or opposite effects of cations like Ca and Mg. For Mo, W, and P

oxide mole fraction are used to quantify the silicate melt effects, whereas for all other elements, the smaller melt composition effects are quantified with the simpler single parameter, NBO/T. It is clear that silicate melt is crucial to quantify for every element, and it needs to be done for FeO bearing systems that approach peridotite (e.g., Al- and Ca-poor, Mg-rich).

**Issue 2:** Pressure causes melt structural changes. Several recent studies have concluded that changes in D(met/sil) at higher pressure are due to structural changes in silicate melts. In the case of D(Ni) and D(Co) [10] argues that the partition coefficients decrease, but there is a slope change at 5-10 GPa. In the case of D(W) [13] argue that D(W) changes from a positive slope to a negative slope at higher pressures. There are alternate explanations for both: [10] dataset is not for constant composition: melts change composition and the change correlates with pressure. Whereas the [13] D(W) data is not for variable pressure alone – it is for variable P and T and these two variable will cause a change in slope in D(met/sil) for many elements when only pressure is plotted. This happens independently of melt structure and it is consistent with a simple volume change for the metal-oxide equilibrium across variable P and T. True melt structural changes for silicate melts relevant to Earth's mantle have only been observed at higher pressure conditions (>20 GPa), and for MgO-rich melts, not the basaltic melts used in the studies of [10] and [13].

**Issue 3:** Primitive upper mantle (PUM) does not consider relevant deep mantle phases. Some elements are compatible in deep mantle phases, and in fact more compatible than in metal. The best examples are Mn, V and Cr, all of which are compatible in deep mantle phases such as garnet, magnesio-wüstite, and Mg perovskite [14]. When combined with metal-silicate partition coefficients, these phases can be responsible for the PUM depletions of all three elements, and allow a shallower single stage scenario as will be seen below.

**Updated predictive expression:** The predictive expressions have the form:

$$\ln D = a \ln fO_2 + b/T + cP/T + d(1-X_s) + e(1-X_c) + \sum f_i X_i + g$$

These expressions are guided by the thermodynamics of simple metal-oxide equilibria that control each element, include terms that mimic the activity coefficients of each element in the metal and silicate. Critics of this approach say that it cannot be extrapolated outside of the calibrated range because of violations of the Gibbs-Duhem equation [15]. Although this is true, it is not meant to be a rigorous thermodynamic expression, and

is obviously an empirical approach guided by thermodynamics. In addition, extrapolation far outside of the calibrated database is not done, and others are cautioned against this.

**Results:** Focusing on the four most refractory, and therefore the most robust, elements – Ni, Co, Mo and W – the hypothesis of a single PT core formation event can be tested with the updated regressions. In order for these elements to be explained by metal-silicate equilibrium the  $D(\text{met/sil})$  must be 17, 13, 45, and 17, respectively. Several variables are fixed in the calculations in order to show possible PT space allowing fits to these elements: silicate melt composition is that of primitive upper mantle [16] with 200 ppm S and  $\text{NBO/T} = 2.8$ , metallic liquid with  $X_s=0.05$  and  $X_c=0.12$ , and  $\Delta I W = -2.2$ . Curves for each element can be constructed for the partition coefficient required, and there is a PT range where all four intersect near 32 to 42 GPa, and 2500-2700 K. Copper, Ga, and P are also considered, but uncertainties are higher due to volatility of these elements.

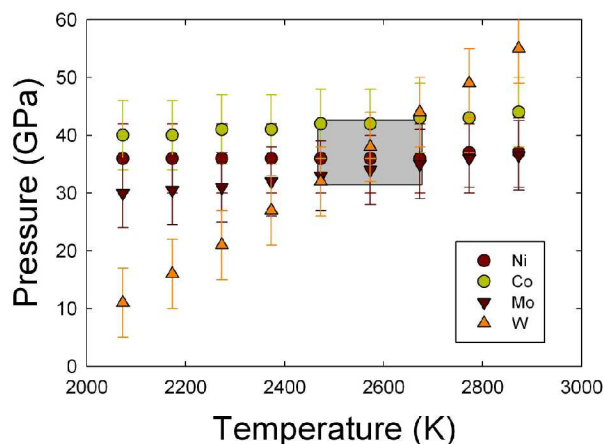


Figure 1: Range of PT conditions over which Ni, Co, Mo, and W have metal-silicate partition coefficients required for a metal-silicate equilibrium scenario. Error bars reflect the  $2\sigma$  error on each regression. Shaded box is the approximate region of overlap for all four elements.

Furthermore, models [8] which force fit Mn, V and Cr mantle concentrations by metal-silicate equilibrium overlook the fact that at early Earth mantle  $f\text{O}_2$ , these elements will be more compatible in Mg-perovskite and (Fe,Mg)O than in metal. Thus any solution to the PUM concentrations must include these deep mantle phases. This removes the need to fit these three elements at very high PT conditions and allows them to be easily explained in a shallow magma ocean scenario. In fact, all 11 trace elements (Fig. 2), plus Sn, Sb, Ge and Zn, are consistent with the same scenario, making

models with multiple stages and changing oxidation states unnecessary.

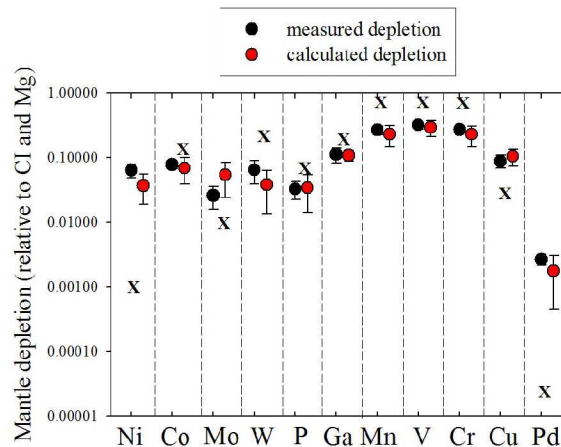


Figure 2: Comparison of measured depletions (black dots; [17]) to calculated depletions at high PT conditions (red dots, this study), and calculated depletions at low PT (1 bar, 1673 K) conditions (X).

**References:** [1] Walker, D. et al. (1993) *Science* 262, 1858-1861; [2] Hillgren, V.J. et al. (1994) *Science* 264, 1442-45; [3] Li, J. and Agee, C.B. (1996) *Nature* 381, 686-89; [4] Ohtani, E. et al. (1997) *Phys. Earth Planet. Inter.* 100:97-114; [5] Righter, K. et al., (1997) *Phys. Earth Planet. Inter.* 100, 115-134; [6] Chabot, N.L. et al. (2005) *Geochim. Cosmochim. Acta* 69, 2141-2151; [7] Wade, J. and Wood, B.J. (2001) *Nature* 409, 75-78; [8] Wood, B.J. et al. (2008) *Geochim. Cosmochim. Acta* 72, 1415-1426; [9] Wood, B.J. et al. (2006) *Nature* 441, 825-828; [10] Kegler, P. et al., (2008) *Earth Planet. Sci. Lett.* 268, 28-40; [11] Righter, K. et al. (2010) *Earth Planet. Sci. Lett.*, in press; [12] O'Neill, H.St.C. et al. (2008) *Chemical Geology* 255, 346-359; [13] Cottrell, E. et al., (2009) *Earth Planet. Sci. Lett.* 281, 275-287; [14] Righter, K. et al., (2006) *Amer. Mineral.* 91, 1643-1656; [15] Wade, J. and Wood, B.J. (2005) *Earth Planet. Sci. Lett.* 236, 78-95; [16] McDonough, W.F. and Sun, S. (1995) *Chemical Geology* 120, 223-254.